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TITLE: Process for continuous spinning of hollow-fiber membranes using a solvent mixture as a precipitation medium

Abstract Text (1):
Microporous hollow fiber polysulfone membranes can be prepared continuously by using a particular combination of casting solution and precipitation solution formulations, and casting conditions. The concentration of components in the precipitation solution are adjusted continuously to maintain original concentrations. The membranes are characterized by high quality, consistent performance and uniform porosity throughout the membrane.

Brief Summary Text (2):
This relates to the preparation of microporous polysulfone membranes using a solvent mixture as a precipitation medium. More specifically, the membranes prepared according to this invention can be spun in a continuous fashion with resulting high quality, consistent membrane performance. These characteristics are achieved by maintaining constant concentrations of components in the precipitation solution. Liquid-liquid membrane precipitation or coagulation is employed.

Brief Summary Text (4):
Polysulfone membranes and hollow fiber membranes are known to the art and have been prepared to a variety of specifications. Hollow fiber membrane fabrication may be accomplished via a wet spinning technique as follows. A casting solution containing a polymer in a solvent is brought into contact with a precipitation solution containing a solvent and a non-solvent. As a result, the polymer precipitates and the membrane is formed. The porous structure and performance of the resulting membrane is determined by the polymer precipitation rate, which is governed by the exchange rate between the solvent and non-solvent. This process causes the concentrations of components in the precipitation bath to vary with the spinning time and therefore effects the polymer precipitation rate. As a consequence, the morphology characteristics, as well as the performance of the resulting membrane, will change with the spinning time.

Brief Summary Text (5):
To overcome the problems associated with the wet spinning process using a solvent mixture as a precipitation medium, a large volume precipitation bath may be employed. The large volume precipitation bath minimizes, but does not avoid, the variation in the concentrations of the precipitation medium. Further, the process becomes more difficult when dealing with large volumes due to high levels of solvent vapor, difficulties in mixing the precipitation solution and temperature control. This is particularly problematic for a continuous spinning process where a solvent mixture is used to precipitate the membrane.

Brief Summary Text (6):
In order to overcome the problems associated with the prior art processes, a new process has been developed wherein the concentration of the components in the precipitation solution are kept constant throughout the spinning process.

Brief Summary Text (10):
It is another object to teach appropriate spinning and setting conditions to allow for the continuous formation of hollow fiber membranes. This is accomplished by

mixing the precipitation solution throughout the spinning process and maintaining the relative concentrations of the individual components of the precipitation solution.

Brief Summary Text (11):
It is another objective to provide a process which is very convenient for scaling up due to a compact design and low levels of solvent vapors. This process is suitable for both small- and large-scale hollow fiber membrane spinning processes.

Brief Summary Text (12):
It is another objective to provide the possibility of variation of compositions in the precipitation bath during the membrane spinning run.

Drawing Description Text (2):
FIGURE 1 is a schematic diagram of one embodiment of the hollow fiber membrane spinning process.

Detailed Description Text (2):
A method of membrane preparation has been discovered by which isotropic polysulfone hollow fiber membranes may be continuously prepared. The continuous process comprises contacting a casting solution with a precipitation solution under conditions wherein the concentration of all components in the precipitation solution are substantially maintained throughout the spinning process. The casting solution comprises a polymer in a solvent for the polymer, and the precipitation solution comprises a solvent for the polymer and a non-solvent for the polymer. During the spinning process, solvent from the casting solution leaks into the precipitation solution causing fiber formation. To maintain concentrations of all components in the precipitation solution throughout the spinning process, non-solvent must be added to the precipitation solution at an appropriate rate depending upon the rate of solvent leakage from casting solution. The rate of non-solvent addition is determined by the following formula r.sub.NSA =(r.sub.SL .div.C.sub.S in PPT)-r.sub.SL. Rate determination is described in greater detail below. Maintenance of precipitation solution component concentrations enables the continual preparation of high quality, highly reproducible hollow fibers which have performance consistency.

Detailed Description Text (4):
The casting solution is extruded directly into a liquid precipitation medium, where formation of the membrane occurs by phase inversion, that is, by precipitation of the polymeric component from the casting solution. This is referred to as liquid-liquid phase separation. In the case of hollow fiber formation, it may also be known as wet spinning. During the initial contact with the precipitation solution, solvent is drawn from the casting solution, increasing the concentration of pore-former and polymer until the increased polymer concentration causes precipitation of the polymer from the casting solution. The membrane continues to form as both solvent and pore-former are leached out and the polymer precipitates completely.

Detailed Description Text (5):
The factors influencing membrane porosity, pore size and overall morphology are exceedingly complex. It has been discovered that a particular combination of these factors, i.e., casting solution, precipitation solution and spinning conditions, will yield an isotropic polysulfone microporous hollow fiber membrane. By "isotropic" is meant that the porosity of the membrane is uniform from one side to the other. The membrane is skinless. The membranes of this invention can be prepared using polysulfone as the sole polymeric component, or using a combination of polysulfone with other polymers.

Detailed Description Text (9):
Polymers or prepolymers such as these are added to the polysulfone polymer in order to modify the structure and surface characteristics of the polysulfone membrane. The additional polymer or prepolymer becomes an integral part of the membrane structure. Polysulfone alone is very hydrophobic. Addition of a polymer or prepolymer such as those described above renders the membranes more hydrophilic than they would otherwise be. Moreover, addition of the BIOPOL.TM. polyurethane prepolymers results

in membranes with increased resistance to nonspecific protein adsorption as well as enhanced biocompatibility. Whereas the polysulfone polymer precipitates out of the casting solution, a polyurethane prepolymer actually polymerizes upon contact with the aqueous precipitation solution.

Detailed Description Text (18):
The precipitation or coagulation mechanism of membrane formation is affected by the composition of the precipitation solution as well as that of the casting solution, and the composition of these two solutions are interdependent. In this disclosure, the terms "precipitation solution," "coagulation solution," "gelation solution,""quench solution" and "quench bath" are used interchangeably to refer to the solution in which the membrane is formed. For formation of hollow fiber membranes, both an outer and a center precipitation or quench solution will be employed. The precipitation solution is made up solvent, non-solvent and an optional swelling agent (also a non-solvent). Together, these components control the rate of membrane precipitation as well as the membrane characteristics, resulting in formation of the isotropic hollow fiber membrane of this invention.

Detailed Description Text (23):
In utilizing the method of this invention to prepare hollow fiber membranes, the precipitation solution used for the outer quench bath can be the same or different from that used for the center quench fluid. In hollow fiber production, the center quench and outer quench are different phenomena. At center quench, a small volume of solution is used, which is almost in a static mode as compared with the casting solution. Conversely, the outer quench bath is present in larger volumes and in a dynamic mode. By controlling the solvent content of the two quench solutions, the phase inversion rate is controlled so as to produce an isotropic membrane. Solvent diffusion out of the casting solution will occur at a different rate at the inner and outer surfaces if the same precipitation solution is used. By adjusting the solvent and swelling agent content of the two solutions, the precipitation (or phase inversion) rate will be equilibrated, resulting in an isotropic membrane.

Detailed Description Text (24):
Hollow Fiber Spinning Conditions

Detailed Description Text (25):
In preparing hollow fiber membranes of this invention, a liquid-liquid or wet spinning process is used. That is, the casting solution is fed through an extrusion die (spinnerette) directly into a precipitation bath, while simultaneously introducing the center quench fluid through the central aperture of the spinnerette to mechanically maintain the hollow center hole of the fiber. The fiber is fabricated and simultaneously quenched as it is drawn through the precipitation bath. The relative concentrations of components in the precipitation solution are substantially maintained throughout the spinning process. By using this wet-spinning process, fibers with homogeneous pore structure and membrane morphology are produced.

Detailed Description Text (28):
One of the key factors in preparation of the isotropic hollow fiber membranes of this invention is use of the wet spinning process, that is, spinning the casting solution directly into the precipitation solution or bath. In addition, selection of appropriate solutions for the inner and outer precipitation baths is important, as is the appropriate drawing or spinning rate of the fiber as it is formed. The presence of the center quench fluid also allows for simultaneous polymer precipitation from both the inner and outer surfaces of the fiber. The spinning rate is adjusted to allow for exchange of components between the casting and precipitation solutions. The solvent and pore-forming agent are leached out of the casting solution and are replaced by the non-solvent and swelling agent from the precipitation solution. As a consequence, polymer precipitation occurs, leading to formation of the membrane. Once these initial adjustments are made to produce a membrane with the desired morphology, the circulation of fresh precipitation solution as taught by this invention is employed to consistently spin membranes which conform to the desired characteristics.

Detailed Description Text (30):

The precise spinning conditions are adjusted in order to yield hollow fibers meeting the desired physical requirements of inner diameter and wall thickness. Centering of the central aperture of the spinnerette is required in order to achieve a fiber having a uniform wall thickness. Any spinnerette suitable for the preparation of hollow fiber membranes may be used to prepare the membranes of this invention. The spinning conditions left to be adjusted are the flow rate and pressure of the casting solution, and the flow rate and pressure of the center quench fluid. These adjustments are well within the knowledge and ability of one of ordinary skill in this art. The preferred temperature for the casting solution will be in the range of ambient temperatures, although higher temperatures, e.g., up to about 70.degree. C, may be employed to reduce the viscosity of the casting solution.

Detailed Description Text (33):
In the preferred embodiment of this invention, isotropic hollow fiber membranes are prepared according to the process diagrammed in FIG. 1. This process was used in preparing the membranes of Examples 1-3.

Detailed Description Text (35):
At a predetermined rate, calculated as described below, non-solvent solution 60 is drawn through conduit 62 by means of pump 64 into precipitation solution 20. Depending on the length of time of the spinning process and the size of container 58, it may be desirable to have a mechanism for periodically removing a portion of precipitation solution 20 from container 58.

Detailed Description Text (52):
Extended periods of hollow fiber spinning under conditions wherein the non-solvent is not added to the precipitation solution can yield highly variable fibers of questionable or inferior quality due to continuous dilution of the precipitation solution with solvent from the casting solution. By constant or intermittent addition of non-solvent and substantial maintenance of the precipitation solution composition, the high quality of the fibers can be maintained over an indefinite spinning time. Even more important, the physical characteristics of the hollow fiber being produced do not vary appreciably over the course of the spinning. This ability to control the spinning process to produce fibers of uniform characteristics from beginning to end of a spinning run significantly improves the efficiency of the process by reducing hollow fiber wastage.

Detailed Description Text (59):
The isotropic polysulfone-based hollow fiber membranes of this invention will find utility in industrial or pharmaceutical filtration and fractionation processes. These membranes exhibit good tensile strength, high water flux, and high hydraulic flux recovery. Membranes can be prepared which exhibit high rejection of high molecular weight species and low rejection of lower molecular weight species.

Detailed Description Text (89):
Hollow fiber membranes of the invention were prepared following the wet spinning process described above. The overall process is depicted in FIG. 1. A spinnerette with an orifice of 0.1 cm in inside diameter (ID) and a capillary of 0.05 cm in ID was used to spin the fibers. Volumes of precipitation solution in the U-tube container and the reservoir were 18,000 ml and 2,000 ml, respectively.

Detailed Description Text (91):
During the fiber spinning process, the precipitation solution was circulated from the reservoir through the U-shaped container in a flow direction opposite to which the fiber was being drawn, and finally the precipitation solution was returned to the reservoir. The precipitation solution was circulated at a rate of 1 l/min. Non-solvents were added to the precipitation solution at a rate of r.sub.NSA =(r.sub.SL .div.C.sub.S in PPT)-r.sub.SL.

Detailed Description Text (97):
If the non-solvent mixture was not added to the precipitation solution at this rate, then the concentration of NMP in the precipitation solution would increase 1 volume % after every 7.1 hours of spinning (t=(V.times.0.01)+(r.sub.SL.times. 60)). Therefore, after only 7.1 hours the quality of the fibers would not be consistent and would continue to become more inferior as time went on.

Detailed Description Text (99):
The performance of the fibers was evaluated after 3 and 26 hours of spinning, and the properties were nearly identical. Fibers were obtained which had an ID of 510 microns with a wall thickness of 75 microns. The fibers had a narrow pore size distribution with a mean pore size of 0.70 microns. The pure water permeability of these fibers was 4,650 LMH/psi. The protein flux with respect to IgG protein solution (3 g/l) was 2,760 LMH/psi with a quantitative protein passage.

Detailed Description Text (102):
Under these spinning conditions without the addition of non-solvents to the precipitation solution, the concentration of NMP in the bath will increase 1 volume % after every 9.5 hours of spinning (determined as described in Example 1). To maintain the concentration of NMP in the precipitation bath, 0.23 ml/min (r.sub.NSA) of a Water/IPA mixture (50/50 in volume) was added into the reservoir.

Detailed Description Text (104):
Fibers were spun continuously for more than 63 hours without altering the performance characteristics. The fiber's ID and wall thickness were 400 microns and 70 microns, respectively. The fiber obtained has a narrow pore size distribution with a mean pore size of 0.65 microns. Table I shows the performance of the fibers obtained at different spinning times.

Detailed Description Text (107):
Under these spinning conditions, the concentration of NMP in the precipitation bath will increase 1 volume % every 9.5 hours of spinning (determined as described in Example 1). To maintain concentration of NMP in the bath, 0.23 ml/min (r.sub.NSA) of a Water/IPA mixture (50/50 in volume) was added into the reservoir (determined as described in Example 2). Fibers were spun continuously for 24 hours, and the fibers obtained showed a consistency in performance.

Detailed Description Paragraph Table (1):
Casting Solution Composition Udell .TM. 3500 Polysulfone (Amoco) 10 wt % Polyvinylpyrrolidone (MW 10,000) 15 wt % N-methylpyrrolidone (NMP) (C.sub.S in CS) 75 wt % Precipitation Solution Composition NMP (C.sub.S in PPT) 58 vol % Water 21 vol % Isopropanol (IPA) 21 vol % Fiber Spinning Conditions Casting solution flow rate (Q.sub.CS) 0.62 ml/min Inner precipitation solution flow rate 0.92 ml/min Outer precipitation solution flow rate 1.0 l/min Fiber spinning rate 450 cm/min Relative Densities Density of casting solution (d.sub.CS) 1.05 g/ml Density of solvent (d.sub.S) 1.03 g/ml

Detailed Description Paragraph Table (2):
Casting Solution Composition Udell .TM. 3500 polysulfone 12 wt % Polyvinylpyrrolidone 15 wt % NMP (C.sub.S in CS) 73 wt % Precipitation Solution Composition NMP (C.sub.S in PPT) 60 vol % Water 20 vol % IPA 20 vol % Fiber Spinning Conditions CS flow rate (Q.sub.CS) 0.465 ml/min Inner precipitation solution flow rate 0.565 ml/min Outer precipitation solution flow rate 1.0 l/min Fiber spinning rate 450 cm/min Relevant Densities Density of casting solution (d.sub.CS)* 1.06 g/ml Density of solvent (NMP) (d.sub.S) 1.03 g/ml Density of polysulfone (d.sub.PS) 1.24 g/ml Density of polyvinylpyrrolidone (d.sub.PVP) 1.03 g/ml *d.sub.CS = 0.12 (d.sub.PS) + 0.15 (d.sub.PVP) + 0.73 (d.sub.NMP) = 0.12 (1.24) + 0.15 (1.03) + 0.73 (1.03) = 1.06 g/ml

Detailed Description Paragraph Table (3):
TABLE I IgG Data* Spinning Time Water Permeability Permeability Passage (hr.) (LMH/Psi) (LMH/Psi) (%)
12 2900 1070 100 29 2800 1170 100 38 2500 950 100 54 2200 1000 100 59 2500 1100 100 63 2600 1040 100
*Testing Conditions: IgG concentration = 3 g/L Transmembrane pressure = .about.1 psi. Shear rate = 3000, sec.sup.-1 Operating time = 15 min.

Detailed Description Paragraph Table (4):

Casting Solution Composition Udell .TM. 3500 polysulfone 13 wt % Polyvinylpyrrolidone 15 wt % NMP (C.sub.S in CS) 72 wt % Precipitation Solution Composition NMP (C.sub.S in PPT) 60 vol % Water 20 vol % IPA 20 vol % Fiber Spinning Conditions CS flow rate (Q.sub.CS) 0.465 ml/min Inner precipitation solution flow rate 0.565 ml/min Outer precipitation solution flow rate 1.0 l/min Fiber spinning rate 450 cm/min

CLAIMS:

4. The process of claim 3 wherein said outer precipitation solution is circulated in a direction opposite to the hollow fiber spinning direction.

17. The process of claim 16 wherein said outer precipitation solution is circulated in a direction opposite to the hollow fiber spinning direction.